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POSSIBLE USES FOR BACTERIA IN METALLURGICAL OPERATIONS

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POSSIBLE USES FOR BACTERIA IN METALLURGICAL OPERATIONS[1]

by

Joseph A. Sutton[2] and John D. Corrick[3]

INTRODUCTION AND SUMMARY

The prospect of utilizing bacteria in mining and metallurgical processes introduces a new and challenging area of investigation. Elements of bacteriology and metallurgy are discussed in connection with possible areas where biological science might be applied in extractive metallurgy. Bacteria may prove important in the selective separation of metals from ores and metallurgical solutions, the production of sulfur from gypsum or pyrites, and the production of sulfuric acid from elemental sulfur.

A series of reports concerning the experimental applications of bacteria on minerals and metallic ores will follow this paper.

For several years the Bureau of Mines has been investigating the action of bacteria in the oxidation of sulfide minerals and their potential uses in metallurgical processes. Primary attention has been given to the possible utilization of certain strains of autotrophic bacteria that live in industrial leaching solutions or fractures of mineral outcrops. The purpose of this paper is to acquaint the mining and metallurgical engineer with micro-organisms and some of their possible applications in the field of extractive metallurgy.

BACTERIA

The importance of microbes in chemical processes has been long known. In 1862, Pasteur demonstrated that microbes were responsible for the oxidation of alcohol to acetic acid (16)[4]. He also suggested that ammonia might be oxidized to nitrate by a similar process; this conjecture was confirmed by Schloesing and Muntz in 1877 (21).

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[4] Underlined numbers in parentheses refer to items in bibliography at the end of the report.

Layman usually assume that all bacteria are harmful and that the net result of their existence is disease. However, most micro-organisms are harmless, and many are necessary for the survival of other living things. For example, microbes in the soil have been, over the ages, oxidizing and reducing minerals to soluble forms that could be utilized by higher plants. Many sedimentary ore deposits have been formed by the action of micro-organisms (3).

Ever changing natural environmental conditions effect the growth and activity of bacteria. Improper temperature, moisture, acidity, alkalinity, or lack of proper food for energy can reduce the activity of the organisms, cause them to lie dormant, or destroy them. Each strain of bacteria has special requirements for survival and maximum activity.

Autotrophic bacteria (15, 18, 20, 22) appear to be the most important to the field of extractive metallurgy. Organisms of this category obtain energy by oxidizing inorganic compounds of sulfur, iron, and nitrogen, and obtain carbon for cell structure from carbon dioxide. Autotrophic organisms that assimilate carbon dioxide by the aid of radiant energy are photosynthetic; those that reduce carbon dioxide by chemical energy are chemosynthetic. The morphological and physiological characteristics of some of the more pertinent bacteria (2) are described briefly under separate headings.

Nitrifying Bacteria

Chemosynthetic autotrophic nitrifying bacteria derive energy for growth from the oxidation of ammonia to nitrite or nitrite to nitrate. There are several genera capable of oxidizing these compounds. Two of these genera are *Nitrosomonas* which oxidizes ammonia to nitrate ($NH_4 + 1\text{-}1/2O_2 \rightarrow 2H + H_2O + NO_2 + 66$ cal.) and *Nitrobacter* which oxidizes nitrite to nitrate ($NO_2 + 1/2O_2 \rightarrow NO_3 + 17$ cal.). These organisms are either ellipsoidal or rod-shaped and are widely distributed in nature.

Iron Bacteria

The chemosynthetic autotrophic iron bacteria that are of interest to this subject are of the genera *Gallionella*, *Clonothrix*, and *Leptothrix* and the species *Ferrobacillus ferrooxidans* and *Thiobacillus ferrooxidans*. These organisms are commonly found in waters containing iron salts. The three genera are filamentous in appearance. *Gallionella* and *Clonothrix* oxidize ferrous iron in an alkaline medium to form ferric hydroxide sheaths. The formation of these sheaths ultimately brings the death of the organisms and the precipitation of iron. Species of the genus *Leptothrix* also oxidize ferrous iron and form ferric hydroxide sheaths; however, this genus is able to shed the sheaths when they become too thick. In this manner, the iron is precipitated, and the organisms continue their metabolic processes.

F.[5] *ferrooxidans* and *Th.*[6] *ferrooxidans* were recently isolated and identified. They are rod-shaped and in an acidic medium oxidize ferrous iron to ferric sulfate. Th. ferrooxidans is also capable of oxidizing elemental sulfur to the sulfate state.

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[5] *F.* is the abbreviation for the genus *Ferrobacillus*.

[6] *Th.* is the abbreviation for the genus *Thiobacillus*.

Sulfur Bacteria

Sulfur bacteria are widely distributed in nature wherever sulfur or hydrogen sulfide are present: in sulfur springs, sulfur mines, sewage, or swamps.

Species under the genus Desulfovibrio are slightly curved and rod-shaped and form hydrogen sulfide by the reduction of sulfur compounds. The organisms require sulfate or certain incompletely oxidized inorganic compounds as specific oxidizing agents and utilize organic compounds for development. The organic compound acts as a hydrogen donor during the reduction of sulfate to sulfide. These organisms are heterotrophs, not autotrophs, as they require organic compounds for development. They are mentioned because of their unique reduction processes.

Members of the family Chlorobacteriaceae are photosynthetic autotrophic bacteria that contain green pigments of a chlorophyllous nature which are not identical with plant chlorophyll or bacteriochlorophyll. The organisms are oval, vibrio, or rod-shaped. During growth, the bacteria oxidize hydrogen sulfide to free sulfur which is deposited outside the cells. The family Thiorhodaceae are photosynthetic autotrophic bacteria that develop purplish (contain green bacteriochlorophyll) cell aggregates of various sizes and shapes. These bacteria oxidize hydrogen sulfide to sulfuric acid. The hydrogen sulfide acts as a hydrogen donor, and sulfur accumulates as droplets in the cells before it is oxidized to sulfuric acid. Both families are found in water containing hydrogen sulfide and exposed to radiant light.

Chemosynthetic autotrophic bacteria that oxidize hydrogen sulfide and deposit elemental sulfur within their cells may be represented by the genera Beggiatoa, Thiothrix, and Thioplaca. These organisms are threadlike in appearance.

Species under the genus Thiobacillus are rod-shaped chemosynthetic autotrophs and derive their energy from incompletely oxidized sulfur compounds. Th. thiooxidans oxidizes elemental sulfur and thiosulfate directly to sulfate. This species produces more acid from the oxidation of sulfur and tolerates higher acidity than any other species. Th. concretivorus oxidizes elemental sulfur, hydrogen sulfide, and thiosulfate directly to sulfate. They are able to tolerate acid concentrations up to 10 percent. Th. ferrooxidans derives energy from the oxidation of thiosulfate, elemental sulfur, or ferrous iron, and produces solutions of sulfuric acid or acid-ferric sulfate. The pH range of the Th. ferrooxidans' environment approaches that of Th. thiooxidans but does not extend below a pH of 2.

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BACTERIA IN METALLURGICAL AND ALLIED FIELDS

Detrimental Effects

Manganese Ores

Some of the effects of bacteria in metallurgical and allied fields may be far from beneficial. In fact, they may be directly responsible for some metallurgical problems that are still unexplained. Recent observations by the Bureau of Mines at Boulder City, Nev., have shown that unidentified bacteria are in some dry-cell batteries. These bacteria may belong to the genus Nitrosomonas and are responsible for the failure of certain high-grade manganese dioxide ores to pass standard shelf-life performance tests required in dry-cell battery specifications. The function of the manganese dioxide ore is that of an oxidizing agent used to prevent the accumulation of hydrogen gas on the carbon rods of the batteries. Bacteria of the genus Nitrosomonas are able to separate hydrogen from ammonia compounds and, under certain conditions, may be capable of oxidizing ammonia in the electrolyte of the battery to form nitrates, thus releasing hydrogen and causing premature failure of the battery.

Bituminous Coal Mines

Thousands of dollars of mining equipment are destroyed each year by the acid formed within active and abandoned bituminous coal mines of Pennsylvania and West Virginia. The waters issuing from these areas are highly acidic and contain high concentrations of iron which form major pollutants in streams and rivers. The iron and acid are the oxidation products of iron sulfides (pyrite, marcasite, and sulfur balls) associated with the coal. The reactions of iron and sulfur oxidizing bacteria, water, and atmospheric oxygen upon the sulfide minerals are reported responsible for the acidic condition of the mine waters (8, 12, 13, 14).

Application In Metallurgical Processes

Selectively Separating Metals

Microbes have played an important role in the formation of many sedimentary deposits of calcium, iron, sulfur, manganese, aluminum, copper, vanadium, and phosphorus-bearing minerals by either oxidation and reduction, erosion and precipitation, elemental accumulation and dissipation, or by contributing their inorganic remains to its mass (1). A systematic investigation of various strains of bacteria that have contributed to the formation of these deposits and a study of factors which control the physical and biological conditions affecting the reactions could provide information on selectively separating metals and nonmetals from ores and metallurgical solutions by bacterial action.

Sulfur Production

Several lakes in a stretch of salt marsh in Western Libya were discovered to contain sedimentary deposits of elemental sulfur (6). The formation of these deposits has been described as being the handiwork of countless sulfate-reducing and photosynthetic sulfur bacteria (10). British scientists, working with strains of sulfate-reducing bacteria isolated from several of these lakes, have produced 10 ounces of sulfur from 5 pounds of calcium sulfate (gypsum) mixed with 50 tons of sludge (7). Small-scale plant studies for producing sulfur microbially from gypsum were proposed (11). However, due to the slowness of the work and the resulting time needed to produce technical papers on the subject, the Research Council of the Department of Scientific and Industrial Research discontinued the study (7).

The vast gypsum deposits in the United States and the importance of sulfur to our economy certainly justify the extension of the research in this direction. There is a possibility that waste products from the food processing industry could be utilized as inexpensive hydrogen donors by the genus Desulfovibrio for the reduction of calcium sulfate (gypsum) to hydrogen sulfide. The hydrogen sulfide then could be oxidized to elemental sulfur by photosynthetic bacteria.

Another potential source of elemental sulfur in this country is in the form of pyrites (pyrite, marcasite, and pyrrhotite). The iron-oxidizing bacteria Th. ferrooxidans and F. ferrooxidans are known for their ability to oxidize iron in the ferrous form. If these organisms could metabolize the iron in pyrite minerals, there is a possibility that elemental sulfur would be liberated.

Sulfuric Acid Production

The sulfur-oxidizing bacteria Th. thiooxidans and Th. concretivorus are capable of producing and remaining active in acid concentrations up to 10 percent. Sulfuric acid in concentrations within this range has many applications in the metallurgical industry. If a bacterial process for producing sulfuric acid at the mine site in the volume and concentrations required could be developed, a much smaller capital investment would be necessary than is now required for a conventional sulfuric-acid plant. The chief requirements necessary for the organisms to react and produce acid are water, sulfur, heat (18° to 30° C.), and a natural open basin.

Leaching Low-Grade Ores

In recent years, scientists have achieved varying degrees of success in extracting molybdenum (3), manganese (17), and zinc (19) from low-grade ores with bacteria isolated from soil and acid mine waters. In 1954 L. C. Bryner (4) reported that the copper in effluent waters of the Bingham Canyon, Utah, open-pit mining operation, that had been attributed to atmospheric oxidation of the sulfuritic materials of the ore, was at least partially due to the action of micro-organisms native to the ore deposit. Based on this discovery and experimental work conducted by the Kennecott Copper Corporation, a patent for extracting copper, molybdenum, and zinc from ores was granted in 1958 to S. R. Zimmerley, and others (23). The patent also covered the upgrading of chromite ores and titanium-bearing material.

Sulfuric acid and acid-ferric sulfate solutions are employed as metal solvents in hydrometallurgy processes for leaching copper and other metallic ores. The bacteria Th. thiooxidans, Th. concretivorus, and Th. ferrooxidans are capable of producing sulfuric acid, whereas the bacteria Th. ferrooxidans and F. ferrooxidans produce solutions of ferric sulfate. The presence of these iron and sulfur-oxidizing bacteria in waters issuing from the leaching areas of several low-grade copper deposits indicate that the organisms may be assisting in extracting copper (11). However, it is not known how effective these organisms are in producing acid-ferric sulfate solutions under the conditions surrounding ore deposits. Before the importance of these bacteria in leaching processes can be ascertained, it is necessary to determine whether the organisms are able to utilize the iron and sulfur occurring in sulfide minerals (chalcopyrite, pyrite, bornite, chalcocite, and covellite) or are relying on some means such as atmospheric oxidation to free the necessary elements.

A clear understanding of how pure strains and combinations of strains react on low-grade ores should suggest ways in which the metallurgical industry could capitalize on bacterial actions. By controlling bacterial activity, it may be possible to increase the quantity of metal extracted and simultaneously correct some of the problems (clogging of leaching areas with precipitated iron and the high consumption of scrap iron in cementation launders) now existing in leaching operations. It may also be possible to leach profitably many ore deposits that have been considered too low in mineral content for practical mining.

A study is to be undertaken on each of the proposed phases of extractive metallurgy presented in this paper. The first Report of Investigations will cover the effect of Th. thiooxidans on extracting metals from selected ores and minerals.

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